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Structural Characterization of GaN Nanowires Fabricated via Direct Reaction of Ga Vapor and Ammonia

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ABSTRACT

We report structural studies of large-scale wurtzite GaN nanowires fabricated by direct reaction of Ga vapor and NH_3. This recently reported growth technique [1] demonstrates processing of GaN one-dimensional structures as thin as 26 nm and up to 500 μm in length. This method is both interesting and attractive in that fabrication is carried out without the assistance of template materials as required by other methods. In this study, transmission electron microscopy (TEM) is used to characterize the nanowires, while x-ray diffraction (XRD) and energy dispersive x-ray spectroscopy (EDS) data provide supporting structural/compositional analysis. Our structural investigation reveals the presence of thin hexagonal platelets, which we believe play a critical role in the nucleation, growth, and orientation of the wires. In particular, our findings indicate that most of the wires grow along the $[2\bar{1}\bar{1}0]$ direction, normal to the platelet edges.

INTRODUCTION

Since Han et al. first demonstrated the synthesis of Gallium Nitride (GaN) nanorods through a Carbon Nanotube-confined reaction [2], there has been increasing interest in finding novel fabrication techniques. Nanometer sized one-dimensional structures of various materials has potential uses in the development of nanodevices and for basic mesoscopic research [3,4]. GaN is particularly promising due to its large band-gap and high melting point, and is already being used in blue LEDs, laser diodes, and for high temperature electronic devices. Following Han's publication in 1997, Cheng et al demonstrated the synthesis of wurtzite GaN in alumina membranes [4]. In addition, Duan et al [5], grew pure $[01\bar{1}0]$ oriented wires using a laser-assisted catalytic method. Here, laser ablation of a GaN-catalytic metal composite target generated reactive sites confining and directing the growth of crystalline wires. There has now been a growing number of reports on methods to fabricate nanowires of GaN and other materials [6-10]. However, these methods have all required the use of catalysts or templates. The technique used in this work (described in the next section) demonstrates a catalyst/template free nanowire fabrication route through the direct reaction of Ga and flowing Ammonia in a tube furnace.

EXPERIMENT

The schematic diagram shown in Figure 1, illustrates the basic experimental set-up used in this work. Approximately 3 g of pure Ga metal was placed in a Boron Nitride boat which was set at the bottom of a horizontal oven. The tube of the oven was lined with a

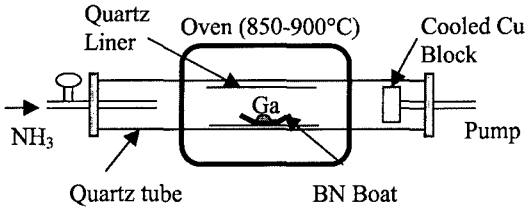

Figure 1. Experimental set-up for direct reaction of Ga vapor and Ammonia.

quartz or BN liner for protection against contamination during growth. Ammonia was injected into the tube through a mass-flow controller (MKS Instruments, Inc., model 1259B) at rates ranging from 50-100 sccm. The total upstream pressure was kept constant at 15 Torr. For GaN nanowire synthesis, the temperature in the oven was varied between 850-900 °C for 3-4 hrs. GaN is formed through the reaction [11],

$$2Ga + 2NH3 \rightarrow 2GaN + 3H2\uparrow$$

so that the overall growth kinetics are influenced by the amount of ammonia and Ga at the growth surface. The resulting reaction products were collected from the cooled Cu block (see Figure 1), BN boat, and quartz liner, and subsequently studied through SEM, XRD, EDS and TEM. TEM samples were obtained by applying small amounts of glue onto Cu mesh grids and contacting them to the reaction products. Subsequent TEM analysis was carried out on a JEOL 4000FX transmission electron microscope operated at 300 KV.

RESULTS AND DISCUSSION

Figure 2 shows an SEM image of the direct-reaction products for samples grown for 4 hrs at 900 °C and an NH_3 flow rate of 80 sccm. Polycrystalline GaN hillocks tend to form spontaneously, while thin nanowires grow on top of the hillocks. These polycrystalline hillocks are believed to play a critical role in the nucleation and growth of the wires. SEM images reveal wires as long as 500 μm. SEM images also showed what appeared to be mostly amorphous material from samples collected from the cooled copper block, compared to those collected from the BN boat and liner.

Overall structural information from these reaction products were obtained through standard θ-2θ XRD Bragg scans. Figure 3 shows typical Bragg scans obtained from samples collected from the BN boat and cooled Cu Block. For comparison, these samples were placed on Si substrates so that XRD data could be normalized under the Si (400) substrate peak. Strong peaks corresponding to a wurtzite GaN pattern were obtained from the samples collected from boat and liner, while much lower peak intensities were obtained from the samples collected from cooled Cu block. This confirms that a relatively low density of crystalline material is formed on the Cu block.

To confirm the overall purity and composition of the reaction products, a JEOL 8900 superprobe was used to carry out energy-dispersive x-ray analysis. Though the resolution of this instrument was not sufficient to isolate and analyze a single wire, an informative analysis

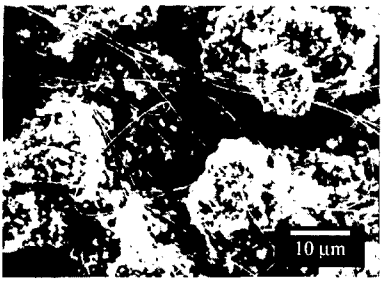

Figure 2. SEM image of reaction products showing polycrystalline hillocks and nanowires.

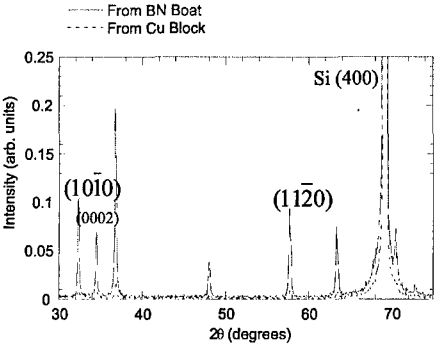

Figure 3. XRD Bragg scan of reaction products can be indexed to GaN wurtzite structure.

of selected areas was nonetheless carried out. That is, areas containing only the surrounding hillocks and areas containing both hillocks and nanowires were studied. EDS scans revealed both these areas to be very pure as evidenced by the strong Ga k_α peaks in the scan shown in Figure 4. Strong N peaks were also revealed, confirming the purity of the reaction products.

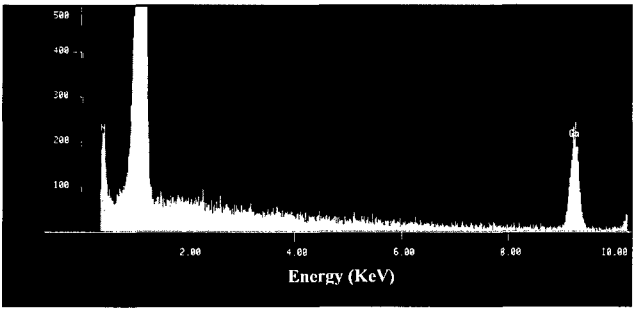

Figure 4. EDS spectrum (Counts vs. x-ray energy), of area containing at least one nanowire and surrounding area (hillocks).

TEM Analysis

Figure 5 shows TEM images of the two main types of wires observed in the reaction products. The first (Figure 5a), shows a wire with a diameter of approximately 26 nm and its (0001) selected area diffraction pattern (inset). This (0001) diffraction pattern confirms the wire has the wurtzite structure and interestingly, reveals the growth direction to be [2$\bar{1}\bar{1}$0]. While most of the wires seem to share this growth direction, a few wires exhibit features that suggest otherwise. Figure 5b shows a ~122 nm diameter wire with facets along the growth direction. Each of the two facets lie approximately 30 nm from the edge suggesting that this

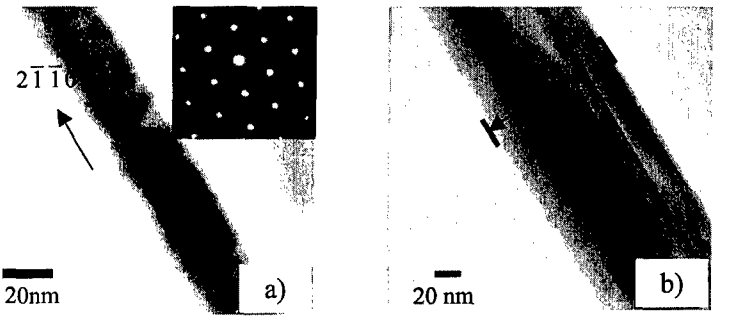

Figure 5. a) TEM image and (0001) DP (inset) showing 26 nm diameter wire. b). TEM image showing ~122 nm wire with facets parallel to growth direction.

particular wire actually grows in the [0001] direction. However, further analysis via precise zone axis diffraction patterns (ZAP) is needed to confirm the growth direction in these particular wires. The reaction products are oriented randomly on TEM grids, making it difficult to obtain precise ZAP analysis of the nanowires.

TEM analysis was also used to gain a better understanding of the polycrystalline hillocks observed in the SEM images. These hillocks were shown to be composed of thin (and electron transparent) hexagonal platelets with the [0001] direction normal to the surfaces. Several nanowires were found to originate from the edges of the thin crystal platelets as shown in Figure 6. These images confirm that the wires do indeed grow in the

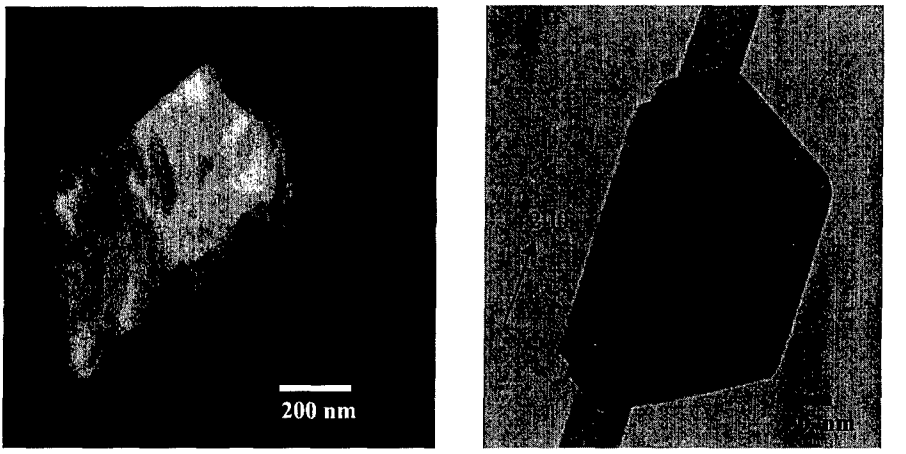

Figure 6. TEM images showing wires that were found to originate or grow from the edges of thin hexagonal platelets and along the [$2\bar{1}\bar{1}0$] directions.

[$2\bar{1}\bar{1}0$] direction, indicating that preferential nucleation and faster growth takes place along platelet edges rather than platelet faces. This is quite different from GaN nanowires reported in other studies [6-8], where growth directions are typically [$01\bar{1}0$] or [100] (in the three index system).

CONCLUSIONS

In summary, the fabrication of GaN nanowires through a direct reaction of Ga and flowing ammonia was demonstrated. SEM images showed that the reaction products consist of polycrystalline hillocks and wires with lengths exceeding 500 μm. EDS, XRD, and SAD showed that the wires are pure GaN with the wurtzite structure. TEM analysis showed that the hillocks consist of thin hexagonal platelets from which the wires tend to nucleate and grow. In particular, most wires grow along the [$2\bar{1}\bar{1}0$] directions, out of the hexagonal platelet edges. Thicker wires tend to show facets along the length and suggest a [0001] growth direction, or out of the platelet faces. Current work in progress includes structural analysis at the tips of the wires via high-resolution imaging to understand the overall growth mechanism. Much work is still needed to fully understand how and why nanowires grow through this relatively simple fabrication technique. Work is also underway to investigate the effect of several processing parameters including temperature and ammonia flow rate on the length and diameters of the wires [12].

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